Dendritic incorporation of quinacridone: solubility, aggregation, electrochemistry, and solid-state luminescence†

Adrian Ortiz, Ware H. Flora, Gemma D. D'Ambruoso, Neal R. Armstrong* and Dominic V. McGrath*

Received (in Corvallis, OR, USA) 3rd September 2004, Accepted 20th October 2004
First published as an Advance Article on the web 8th December 2004
DOI: 10.1039/b413684e

The first incorporation of quinacridone, a technologically important organic electroluminescent emitter, into dendrimers increases solubility, decreases aggregation, retards heterogeneous electron transfer, and enhances luminescence in condensed phases (powders and thin films).

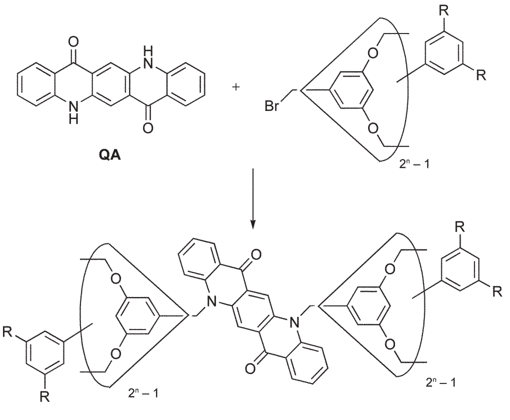
The linear *trans*-quinacridone (QA) chromophore[1] demonstrates promising photovoltaic and photoconductive properties and has become an important dopant dye emitter in electroluminescent display devices.[2,3] Dopant dyes are widely used in small molecule and polymeric organic light-emitting diodes (OLEDs) to enhance the electroluminescence (EL) efficiency through both Förster energy transfer (ET) and charge transfer/recombination (CT) pathways.[4–6] However, self-quenching and aggregation are problems for many dopant dyes, including quinacridone, resulting in significant decreases in luminescence efficiency. Modification to isolate guest emitters, while maintaining high rates of energy and charge transfer with the surrounding medium, is critical.[7,8] Alkylation at the N,N′ positions of quinacridone inhibits aggregation of the dopant dye in aluminium quinolate-based (Alq_3) OLEDs.[4] However, our own recent work on *N*,*N*′-diisoamylquinacridone (DIQA), which is less aggregating than *N*,*N*′-dimethylquinacridone, still indicates aggregation at higher concentrations and in neat thin films.[5,6] Herein we report the dendritic encapsulation[9–11] of quinacridone by *N*,*N*′-disubstitution of the chromophore with two types of benzyl aryl ether dendrons. With increasing generation, these materials exhibit enhanced solubility in organic solvents, sharply declining rates of heterogeneous electron transfer in solution, and lower tendency toward chromophore self-aggregation in thin films that results in dramatically enhanced thin film luminescence.

Incorporation of quinacridone into the core of benzyl aryl ether dendrimers was accomplished by alkylation of the vinylogous amide nitrogens with zeroth through third-generation dendritic bromides[12,13] (Scheme 1). Dipolar aprotic solvent conditions (NaH/DMF) proved successful for only the lowest-generation quinacridone dendrimers (Method A) (ESI†). First-generation **1** and zeroth-generation **4** were obtained in 41 and 94% yields, respectively. However, use of these conditions to prepare higher-generation dendrimers yielded predominately mono-*N*-alkylated quinacridones. Much more successful were previously reported[14] heterogeneous conditions (aqueous NaOH/toluene) in the presence of a phase transfer catalyst (TBAI) that provided dendrimers **2–7** in moderate to good yields (Method B) (ESI†).

All compounds were structurally characterized by a combination of ^{1}H NMR, mass spectrometry (MALDI) and gel permeation chromotography (GPC). GPC analysis of **1–7** verified the expected increasing hydrodynamic volume with increasing generation for each dendrimer series. No evidence of solution aggregation was observed.

Dendritic encapsulation of quinacridone was successful in increasing solubility in organic solvents, a critical parameter for solution processing techniques. Quinacridone dendrimers **1** and **2** exhibited enhanced solubilities in chlorinated solvents (CH_2Cl_2 and $CHCl_3$) and **3** was also readily soluble in solvents such as THF, DMF, DMSO and NMP. The peripheral 3,5-di-*tert*-butylphenyl groups on quinacridone dendrimers **4–7** generally rendered these compounds soluble in an even wider range of organic solvents. While zeroth-generation **4** was still only soluble in chlorinated solvents, first-generation **5** was also soluble in THF, NMP and ethyl acetate, and the range of good solvents for second- and third-generation dendrimers **6** and **7** included DMF, diethyl ether and acetone.

Absorbance and photoluminescence (PL) spectra (λ_{ex} = 490 nm) of a dilute solution of **6** are representative of the spectra of all materials presented herein (Fig. 1). Essentially identical spectra (λ_{max} = 513 nm with Stokes shifts of *ca.* 14 nm) were obtained for dilute solutions of all other dendrimers, with luminescent quantum



R = H	R = t-Bu
1: (n = 1) **2**: (n = 2) **3**: (n = 3)	**4**: (n = 0) **5**: (n = 1) **6**: (n = 2) **7**: (n = 3)

Scheme 1 Synthesis of dendritic quinacridones.

---

† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for quinacridone dendrimers: Fig. S1: PL efficiency of neat thin films of dendrimers 4–7 relative to DIQA. Fig. S2: Cyclic voltammograms of 1–7. See http://www.rsc.org/suppdata/cc/b4/b413684e/

*nra@u.arizona.edu (Neal R. Armstrong)
mcgrath@u.arizona.edu (Dominic V. McGrath)

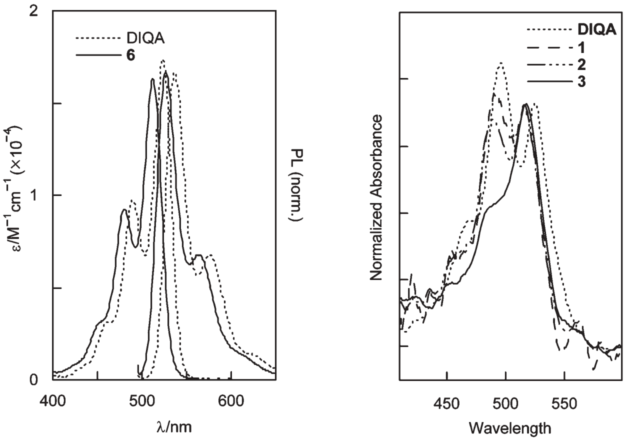


Fig. 1 (Left) Solution (CH$_2$Cl$_2$) absorption and photoluminescence spectra of second-generation **6** and DIQA. (Right) Normalized absorbance spectra of thin films of DIQA and dendrimers **1–3**.

yields, $\phi_f = 0.85$ for DIQA and **1–3** and $\phi_f =$ *ca.* 1.0 for **4–7**. Beer's law plots were linear for all materials up to concentrations of *ca.* 10^{-3} M, indicating no solution aggregation in this concentration regime.

Thin films (*ca.* 40 nm thickness) of DIQA and **1–7** were prepared on glass to investigate the nature of the interaction between quinacridone chromophores in the condensed state. Comparison of normalized absorbance spectra of films of DIQA and **1–3** suggest that DIQA, **1** and **2** are aggregated (blue-shifted absorbance) while the spectrum of **3** approaches that of the unaggregated dilute solutions (Fig. 1). A similar trend is seen with increasing generation for dendrimers **4–7** (Fig. 2), with **4** and **5** slightly aggregated and **6** and **7** predominantly unaggregated. The accompanying PL spectra of the neat thin films of **4–7** (Fig. 2) also approach the shape and position of the solution spectrum as generation is increased, although residual excimer (red-shifted) emission exists for **7** in these highly-concentrated molecular films. The impact of this decreasing tendency to aggregate in the solid state as generation number increases is a logarithmic increase in relative PL efficiency of the neat films, up to a value 6.8 times that of DIQA for **7**.† These changes are consistent with qualitative observations of bulk powders of **4–7** under UV illumination (Fig. 2). Luminescence intensity becomes greatly enhanced as generation (MW) is increased and the photo-induced emission shifts from red to green across the series due to decreased self-absorption and less excimer (red-shifted) emission.

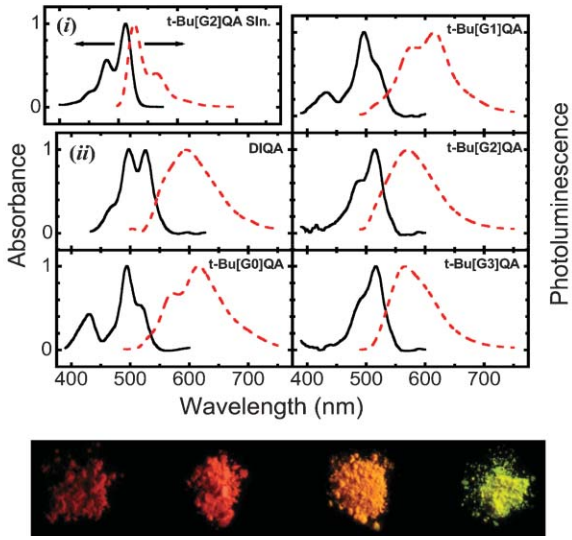


Fig. 2 (Top) Normalized absorbance and luminescence spectra of DIQA and dendrimers **4–7**. (i) Solution spectra of **6**; (ii) absorbance and photoluminescence spectra of neat thin films of DIQA and **4–7**. Thin film absorbance spectra have been baseline subtracted to emphasize the visible band. (Bottom) Bulk powders of **4–7** under UV excitation (365 nm).

Dendrimer series **1–3** and **4–7** exhibit attenuation of electron transfer rates with increasing generation. The formal potentials for first and second one-electron oxidation and reduction processes (Table 1) are not significantly changed from DIQA to **1–6**. However, diffusion coefficients, D_0, and standard rates for heterogeneous electron transfer, k°,‡ for the one-electron oxidation of these materials, decrease approximately an order of magnitude from DIQA to third-generation **3** and second-generation **6**, consistent with previous studies of other dendrimers with redox-active cores, where no electrochemical interaction exists between the core and the dendrons.[9,10] Note k° is up to 2.5 times slower at each dendrimer generation for **4–6** *vs.* **1–3**, suggesting that the *tert*-butyl groups play a significant role in site isolation and retardation of solution heterogeneous electron transfer.

We also note that attenuated solution heterogeneous electron transfer rates with increasing dendrimer size surrounding a redox-active core[9–11] suggests that dendritic encapsulation may be detrimental to energy harvesting of quinacridone dopants by CT pathways in a device architecture. However, in preliminary studies of ITO/PVK–Alq$_3$/Al single-layer OLEDs doped with **4–7** comparisons between PL and EL spectra indicate only a small attenuation of these CT pathways, suggesting that the PVK poly(vinylcarbazole) host can achieve close proximity to the dendrimer core, and high rates of hole-trapping as a consequence, leading to Alq$_3$ emissive state production.[15]

In summary, dendrimerization of quinacridone successfully inhibits aggregation and self-absorption between core molecules in the solid state, with corresponding increases in luminescence efficiency. Further studies using these dendrimers as OLED dopants, especially in wet-processed films, are underway.

This work was supported by the NSF STC-MDITR (DMR-0120967). W. H. F. and A. O. gratefully acknowledge support from Pfizer. D. V. M. is a Dreyfus Teacher–Scholar.

Table 1 Electrochemical data[a] for quinacridone dendrimers

	MW/ g mol^{-1}	$E^{\circ\prime}_{\mathrm{Ox}}$/ V	$E^{\circ\prime}_{\mathrm{Red}}$/ V	$10^6 D^0$/ cm^2 s^{-1}	$10^3 k^\circ$/ cm s^{-1}
DIQA	452.60	0.73	−1.72	14	11
1	917.07	0.78	−1.75	2.7	3.4
2	1766.06	0.76	—[b]	—[b]	—[b]
3	3464.05	0.75	—	1.5	1.5
4	717.01	0.76	−1.78	5.7	4.8
5	1365.93	0.79	−1.75	2.6	2.9
6	2663.79	0.83	−1.70	1.7	1.2
7	5259.49	—	—	~0.84[c]	~0.6[c]

[a] CH$_2$Cl$_2$ solutions at 293° K with 0.1 M TBAHFP supporting electrolyte. [b] Anomalous low solubility precluded measurement. [c] Extrapolated from values for **4–6**.

Adrian Ortiz, Ware H. Flora, Gemma D. D'Ambruoso,
Neal R. Armstrong* and Dominic V. McGrath*
Department of Chemistry, University of Arizona, Tucson,
AZ 85721-0041, USA. E-mail: nra@u.arizona.edu;
mcgrath@u.arizona.edu; Fax: 520-621-8407; Tel: 520-626-4690

Notes and references

‡ D_0 was measured from the peak current (i_p) of the anodic potential sweep through the first oxidation. k° was measured using the Nichelson and Shane treatment of measuring the peak separation (ΔE_p) as a function of scan rate (v). Mass transport by semi-infinite linear diffusion was confirmed from the linearity of plots of i_p *vs.* $v^{1/2}$.

1 G. Lincke, *Dyes Pigm.*, 2002, **52**, 169–181.
2 For leading references: S. De Feyter, A. Gesquiere, F. C. De Schryver, U. Keller and K. Müllen, *Chem. Mater.*, 2002, **14**, 989–997.
3 G. E. K. Y. Jabbour, S. E. Shaheen, J. F. Wang, M. M. Morrell, B. Kippelen and N. Peyghambarian, *Appl. Phys. Lett.*, 1997, **71**, 1762–4.
4 J. Shi and C. W. Tang, *Appl. Phys. Lett.*, 1997, **70**, 1665–1667.
5 S. E. Shaheen, B. Kippelen, N. Peyghambarian, J. F. Wang, J. D. Anderson, E. A. Mash, P. A. Lee, N. R. Armstrong and Y. Kawabe, *J. Appl. Phys.*, 1999, **85**, 7939–7945.
6 W. H. Flora, H. K. Hall and N. R. Armstrong, *J. Phys. Chem. B*, 2003, **107**, 1142–1150.
7 A. W. Freeman, S. C. Koene, P. R. L. Malenfant, M. E. Thompson and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2000, **122**, 12385–12386.
8 T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, J. R. Lawrence, I. D. W. Samuel, S.-C. Lo and P. L. Burn, *Org. Electron.*, 2003, **4**, 71.
9 C. B. Gorman and J. C. Smith, *Acc. Chem. Res.*, 2001, **34**, 60–71.
10 C. S. Cameron and C. B. Gorman, *Adv. Funct. Mater.*, 2002, **12**, 17–20.
11 S. Hecht and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2001, **40**, 74–91.
12 B. Forier and W. Dehaen, *Tetrahedron*, 1999, **55**, 9829–9846.
13 F. Zeng, S. C. Zimmerman, S. V. Kolotuchin, D. E. C. Reichert and Y. Ma, *Tetrahedron*, 2002, **58**, 825–843.
14 L. L. Pushkina, O. P. Shelyapin and S. M. Shein, *Chem. Heterocycl. Compds.*, 1986, **21**, 792–795.
15 W. H. Flora, A. Ortiz, D. V. McGrath and N. R. Armstrong, in preparation.